PROCESS FOR MONITORING THE GASEOUS
ENVIRONMENT OF A CRYSTAL PULLER
FOR SEMICONDUCTOR GROWTH

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority from U.S. Provisional Application Serial No. 60/257,646, filed on December 22, 2000, which is hereby incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

The present invention generally relates to the production of a semiconductor grade material. More specifically, the present invention is directed to a process for monitoring the gaseous environment within a crystal puller, such as that employed for single crystal silicon growth, by means of periodic sampling and analysis. Such a process enables the initiation or start-up of the growth process to be more efficiently automated. Additionally, the process enables the early detection of changes in growth process conditions resulting from, for example, a loss of vacuum integrity within the crystal puller or the aging or decomposition of parts within the puller.

Semiconductor material, such as single crystal silicon used for microelectronic circuit fabrication, is typically prepared by the Czochralski (Cz) method. In this process, for example, a single crystal silicon ingot is produced within the crystal growth furnace chamber of a crystal puller by melting a polycrystalline silicon charge in a fused quartz crucible, dipping a seed crystal into the molten silicon, withdrawing the seed crystal to initiate single crystal growth (i.e., forming a neck, crown, shoulder, etc.), and growing the main body of the single crystal under process conditions controlled to maximize the performance characteristics of wafers obtained from the single crystal ingot. In view of the fact that integrated circuit manufacturers continue to place more stringent

limitations upon silicon wafers obtained from these ingots, it is of particular importance to minimize those instances wherein, during ingot growth, the conditions within the crystal puller are not within acceptable ranges or limits. Process control is also important because such "out of process" growth conditions can and do lower the quality of the single crystal silicon produced, which in turn decreases process throughput and overall process efficiency and economy.

Czochralski crystal growth is a batch-wise process in that, after producing one or more crystals, it is necessary to discontinue the growth process in order to open the crystal puller, for example, to clean the furnace and replace and/or recharge the crucible. Each time the crystal furnace is opened, many of the vacuum seals are broken, which increases the chance that one or more seals will not adequately engage to prevent leaks when the furnace is closed to begin a new production cycle. In addition to leaks which may occur as a result of opening the crystal puller, the continuously varying thermal conditions within the puller during a growth cycle result in ever-changing stress levels on the crystal growth chamber walls, observation ports and piping connections. Occasionally, these changing stresses produce conditions that can compromise vacuum seals or create fractures in welds, thus creating additional air, and in some cases water, leaks.

As a result, before a production cycle is begun, it is important to conduct a "pre-fire" vacuum check to determine whether any leaks are present in the crystal puller, or more specifically to determine if any leaks which are out of the ordinary are present, and thus to ensure the vacuum integrity of the crystal growth furnace. A two-step method for testing the vacuum integrity of the crystal growth furnace is commonly employed. The first step involves reducing the pressure within the crystal puller furnace over a set period of time to confirm that the pumping system is

working satisfactorily. Then, in the second step, the
furnace is isolated from the vacuum pumping system to
measure how well the furnace holds the vacuum and to
determine whether any leaks which are out of the ordinary
are present; that is, once the pressure is reduced, the rate
at which the vacuum pressure is lost over a period of time
(e.g., 10 minutes) is measured to determine if the rate is
out of the ordinary, thus signaling the presence of an
atypical leak. Although this practice can identify a leak,
the procedure requires a significant amount of time to
perform and cannot distinguish the type of leak present or
accurately quantify the amount of a suspect leak in the
furnace. Furthermore, as the use of large diameter furnaces
becomes more prevalent, this practice becomes even less
reliable because the large volume of the furnace makes it
more difficult to detect small, but significant, leaks. In
other words, for large pullers, smaller leaks that can
significantly affect the quality of the material being grown
are not easily detected because these leaks do not
significantly affect the rate at which a large volume
furnace loses vacuum pressure.

The presence of leaks in the crystal furnace, which may
allow the entry of air and/or water, or water vapor, into
the gas stream above or adjacent to the crystal melt, can
result in the loss of crystal puller vacuum integrity, which
in turn leads to "out of process" conditions or problems
during crystal growth. Such "out of process" conditions may
also arise during the growth process because of the natural
deterioration or aging of the crystal puller parts (e.g.,
heaters, heat shields, insulation, etc.). Left unchecked,
such conditions can significantly reduce the efficient
production of an acceptable silicon material. For example,
although carbon monoxide is typically present within the
crystal puller during crystal growth (formed, for example,
by a reaction between the silicon dioxide crucible and the
graphite susceptor, or between silicon oxide (SiO) given off

from the silicon melt and hot graphite parts in the furnace), elevated carbon monoxide concentrations can result from the presence of air or water vapor within the crystal puller. An elevated carbon monoxide concentration can lead to (i) an elevated carbon level in the crystal that is produced, which is detrimental because this can lead to increased oxygen precipitation in wafers obtained therefrom, and (ii) an increase in the amount of oxide particles formed within the crystal puller, which is detrimental because these oxide particles may accumulate on surfaces within the crystal puller to the extent that flakes may break free and fall into the silicon melt, leading to the loss of dislocation-free growth.

Historically, the loss of vacuum integrity, or the occurrence of "out of process" conditions, has not been reliably monitored or detected *during* crystal growth. Although the occurrence of a large air or water leak may be detected during crystal growth if the crystal puller operator observes an increase in the density of an oxide plume from the silicon melt, and/or an increase in the build-up of silicon oxide on hot zone parts within the operator's view, "out of process" conditions affecting crystal growth are typically not detected until *after* the crystal growth cycle is completed. For example, the presence of a high level of carbon monoxide over the silicon melt surface is typically determined or detected by measuring the amount of carbon in the latter portion of the single crystal silicon ingot. Accordingly, if a problem exists, it is not discovered until after an unacceptable product has been made. In fact, because there can be significant time delays before a defectively-grown ingot is sampled and tested, and the results communicated to the operator of the crystal puller, growth of a second unacceptable ingot can occur. As a result, *multiple* defective ingots can be grown before an unacceptable process

condition is identified, resulting in lost resources,
decreased throughput and increased waste.

Accordingly, a need continues to exist for a process by
which the gaseous environment within a crystal puller can be
more efficiently monitored. More specifically, a need
exists for the means by which to more efficiently (i)
conduct pre-fire vacuum integrity tests and (ii) detect
atypical changes in the vacuum integrity and/or the growth
conditions within the crystal growth chamber *during* the
crystal growth process. Preferably, such a process would
provide for the automatic start-up of ingot growth if
conditions (e.g., vacuum integrity) are acceptable for
successful crystal growth, and further would provide for the
real time notification of the crystal puller operator when
an unacceptable growth condition arises. Such an approach
would thus enable the crystal growth process to be altered,
or aborted, before or during crystal growth, thus limiting
waste and increasing throughput or yield.

Summary of the Invention

Among the several features of the invention, therefore,
may be noted the provision of a process for monitoring the
gaseous environment within a crystal puller before and/or
during semiconductor growth; the provision of such a process
wherein vacuum integrity is monitored by means of sampling
and analyzing the gaseous environment within the crystal
puller; the provision of such a process wherein an
atmosphere over the melt and/or the exhaust from the crystal
puller is sampled and analyzed; the provision of such a
process wherein the start-up of the crystal growth process
is automated; the provision of such a process wherein an
atypical leak is detected and characterized (as, for
example, an air leak, a water leak or a purge gas leak); the
provision of such a process wherein the size and location of
an atypical leak are characterized and quantified; the
provision of such a process wherein real-time feedback of

the gaseous atmosphere and/or exhaust are provided to an
operator of the crystal puller; the provision of such a
process wherein elevated levels of carbon monoxide are
indicated during crystal growth; and, the provision of such

5   a process wherein throughput and yield for a given crystal
puller are increased.

Briefly, therefore, the present invention is directed
to a process for monitoring the gaseous environment within a
sealed crystal pulling furnace, used for the growth of an

10   ingot of a semiconductor material in a growth chamber
maintained at a sub-atmospheric pressure. The process
comprises sealing the chamber, reducing the pressure within
the sealed chamber to a sub-atmospheric level, introducing a
process gas into the chamber to purge the chamber and form a

15   gaseous environment therein, and analyzing the gaseous
environment within the chamber for the presence of a
contaminant gas in a concentration which is greater than the
concentration of said gas in the process gas.

Further, the present invention is also directed to a

20   system for use in combination with an apparatus for growing
a semiconductor ingot, wherein the semiconductor growing
apparatus has a growth chamber maintained at a sub-
atmospheric pressure and containing a gaseous environment
comprising a process purge gas. The system comprises a port

25   for withdrawing a sample of the gaseous environment from the
growth chamber; a detector for analyzing the sample for a
contaminant gas in a concentration in excess of the
concentration of the gas in the process purge gas and
generating a signal representative of the detected

30   concentration of the contaminant gas, wherein the detector
receives the sample from the growth chamber via a conduit
connected to the port; and a control circuit receiving and
responsive to the signal generated by the detector for
determining if the detected concentration of the contaminant

35   gas exceeds a pre-set threshold concentration for the
contaminant gas, wherein the control circuit controls the

semiconductor growth apparatus in response to the determination.

Other objects and features of the present invention will be in part apparent and in part pointed out hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1A is a section view of the right side of a Czochralski crystal growth furnace chamber.

Fig. 1B is a section view of the left side of a Czochralski crystal growth furnace chamber.

Fig. 2 is a schematic diagram of one embodiment of a system for quantifying, monitoring and/or controlling growth of a semiconductor material in a Czochralski crystal growth furnace chamber.

Fig. 3 is a graph showing the measured carbon monoxide concentrations for the crystal growth runs A through S, as described further in Example 2.

Fig. 4 is a graph comparing the measured carbon monoxide concentrations within the furnace and exhaust gases for the crystal growth runs A through S, as described further in Example 2.

Fig. 5 is a graph showing the measured carbon concentrations of some of the crystals produced in the crystal growth runs described in Example 2.

Figs. 6a and 6b are copies of photographs taken of two ingots, grown as described in Example 2, while Fig. 6c is a copy of a photomicrograph of a segment of the ingot shown in Fig. 6b.

Fig. 7 is a graph showing the measured nitrogen concentrations within the crystal furnace gases during the pre-fire check before crystal growth runs A through P, as described further in Example 3.

Fig. 8 is a graph showing the measured nitrogen concentrations within the crystal furnace exhaust gases

during the pre-fire check before crystal growth runs A
through P, as described further in Example 3.

Fig. 9 is a graph showing the measured nitrogen
concentrations within the crystal furnace gases during the
crystal growth runs A through P, as described further in
Example 3.

Fig. 10 is a graph showing the measured nitrogen
concentrations within the crystal furnace exhaust gases
during the crystal growth runs A through P, as described
further in Example 3.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the process of the present
invention, it has been discovered that the gaseous
environment within a crystal puller can be monitored by
means of sampling and analyzing that environment to detect:
(i) a loss of vacuum integrity, or a change therein, prior
to or during the growth of a semiconductor material; and/or
(ii) the occurrence of "out of process" growth conditions
during the growth of a semiconductor material. More
specifically, the present invention monitors the gaseous
environment within the growth furnace of a crystal pulling
apparatus and/or the exhaust ports of the furnace, in order
to identify the presence of one or more contaminant gases at
a concentration which is near to, or in excess of, some
unacceptable limit. In this way, the presence of leaks,
which can lead to changes in the vacuum integrity of the
crystal puller before or during the growth process, and/or
changes in process conditions during the growth cycle can be
detected. Such an approach can provide the crystal puller
operator with real time feedback regarding conditions within
the crystal puller environment (e.g., the composition of the
gaseous atmosphere above the melt surface or of the crystal
puller exhaust) prior to and during crystal growth.

The present process thus allows for the start-up of the
crystal growth process to be automated, and further enables

much earlier detection of changes within the crystal puller
environment which can lead to unacceptable growth
conditions. This early detection provides the crystal
puller operator with the opportunity to abort the growth
process or, in some cases, to initiate corrective actions,
at a much earlier stage, thus limiting the amount of
unacceptable silicon which is grown. Additionally,
monitoring the crystal growth environment over time enables
repairs and routine maintenance to be scheduled and
completed much earlier and before an unacceptable condition
arises, therefore effectively preventing unnecessary process
downtime. As a result, the present invention increases
overall process throughput and yield, and therefore overall
process efficiency.

In this regard it is to be noted that, as used herein,
the phrase "vacuum integrity" refers to the ability of the
crystal puller to substantially maintain a typical vacuum
pressure prior to and during crystal growth. Stated another
way, a crystal puller having "vacuum integrity" is
substantially free of atypical leaks in the vacuum seals
present therein, leaks which would otherwise result in an
increase in the concentration of contaminant gases, from the
atmosphere outside the crystal puller, beyond acceptable
levels (as further described herein). While the "typical"
vacuum integrity, or vacuum pressure, may vary from one
crystal puller to the next, this is routinely determined by
means common in the art, such as by statistical process
control ("SPC"), as further described herein below.

It is to be further noted that, as used herein, the
term "out of process" refers to a process condition that is
atypical, unexpected, or out of the ordinary. Again, while
such conditions may vary from one crystal puller or crystal
pulling process to another, "in process" conditions are
routinely determined by means common in the art, such as by
statistical process control. Examples of such "out of
process" conditions include when an upper or lower control

limit, as established by SPC, is exceeded, or when a process
condition, over a statistically significant number of
monitoring cycles, appears to be trending away from what is
typical.

It is to be still further noted that, as used herein,
"real time" is intended to refer to a process wherein
sampling, analysis, and the reporting of results occur
essentially instantaneously; that is, there is essentially
no delay in the time (i.e., less than about 1 second, 0.5
seconds, or even 0.2 seconds) over which samples are
collected, analyzed and reported to the operator. As a
result, there is essentially no difference between the
gaseous environment within the puller at the time the
samples are collected and at the time the results are
reported.

System Design Overview

The present invention will be described within the
context of an exemplary crystal pulling apparatus suitable
for the growth of semiconductor material. More
specifically, the present invention will be generally
described within the context of a Czochralski-type crystal
growth furnace, such as that commercially available from
Kayex of Rochester, NY, designed for the growth of a 300 mm
nominal diameter single crystal silicon ingot. However, in
this regard, it is to be noted that the invention may
likewise be used with any Czochralski-type furnace design
suitable for the growth of various diameters (e.g., nominal
diameters of 150 mm, 200 mm and 300 mm or more) of silicon
and other such semiconductor materials, such as compound
semiconductors (e.g., GaAs).

Referring now to Figures 1A and 1B, the crystal growth
furnace, sealed with the crystal pulling apparatus,
comprises a pulling chamber 50 having a device (not shown)
for lifting and rotating a growing crystal 55, a growth
chamber 51 wherein the polysilicon charge is melted in a

silica crucible 56 supported by a graphite susceptor 57 and
heated by an electrical resistance graphite heater (not
shown). The furnace further comprises a purge tube 60
wherein an inert purge gas 58, such as argon, preferably
flows down the center of the crystal puller 50, over the
growing silicon ingot 55 and is predominantly peripherally
constrained by the inner surface 61 of the vertical wall 62
of the purge tube 60. The purge gas 58 mixes with SiO over
the melt surface 53 and the gas mixture flows peripherally
outward and then upward through an annular region 59 defined
by the outside surface 63 of the purge tube vertical wall 62
and the inner wall surface 57 of the crucible 56. The gas
mixture exiting the annular region 59 as well as purge gas
58 that was not constrained by the purge tube 60 is removed
from the crystal puller 50 via four exhaust outlets 64a,
64b, 64c and 64d arranged so as to be equidistant along the
periphery of the base of the growth chamber. The exhaust
outlets 64a through 64d are in fluid communication with a
vacuum pumping system 70 by a vacuum piping system
comprising two pairs of vacuum pipes 71a and 71b. Each pair
of vacuum pipes is attached to two of the exhaust outlets
64a through 64d and extend into the growth chamber 51 by
graphite extensions lined with silica glass tubes (not
shown). Each pair of vacuum pipes 71a and 71b are reduced
into a right-hand side (RHS) pipe 72 and a left-hand side
(LHS) pipe 73 respectively. The RHS pipe 72 and LHS pipe 73
are subsequently reduced into a main exhaust pipe 76, which
ends into the vacuum pumping system 70. A main exhaust
valve 77 is positioned in the main exhaust pipe 76 prior to
the vacuum pumping system 70.

In operation, the present process samples the gaseous
environment from within the growth furnace, for example, the
atmosphere above the melt surface and/or the gases in the
exhaust from the crystal pulling furnace chamber, and passes
the samples to a detector for characterization and/or
quantification. More specifically, in the context of the

embodiment shown in Figures 1A and 1B, samples of the gas
above the melt (referred to herein as Port 1 samples) are
collected from one or more sample ports 10 positioned
adjacent to the growing crystal 55 within the crystal puller
and samples of the gas in the furnace exhaust (referred to
herein as Port 2 and Port 3 samples) are collected from
sample ports 74 and 75 located within exhaust pipes 71a and
71b respectively.

In this regard it is to be noted that the position of
the sampling ports may be other than herein described. For
example, generally speaking, the ports are positioned at
locations which enable collection of the most representative
samples of gases which the melt surface and growing ingot
"encounter." Additionally, it is to be noted that, although
preferred in some embodiments, the sampling and analysis of
exhaust gases are optional. Experience to-date indicates
sampling in this location can be beneficial, for example, in
characterizing the source or cause of "out of process"
growth conditions in the growth chamber.

It is to be further noted that, depending on the
diameter of the crystal puller and/or other dimensions of
the crystal growth furnace, it may be preferable to monitor
the gases from within the crystal growth furnace at more
than one sample port 10, particularly when gas flow within
the chamber is not uniform above the melt. In any case,
when positioning sample port(s) 10 within the growth
furnace, the sample port(s) is preferably located
sufficiently far from the direct flow of purge gas 58 or any
known sources of common air leaks (for example, the
polysilicon feed tube), such that the collected samples are
not diluted or would otherwise not be representative of the
gaseous environment adjacent to the growing crystal. In a
particularly preferred embodiment, sample port 10 is
positioned above the section of the purge tube 60 wherein
the flow of purge gas 58 is not constrained within the purge
tube 60 as described above. This is preferable, for

example, because the flow of purge gas in this region tends
to develop eddys 65 which, over time, may further
concentrate any contaminant gases which may be present above
the crystal melt before such gases can be delivered to the
furnace exhaust. Therefore, in this sense, samples
collected from this "eddy region" may be more likely to
indicate a loss of vacuum integrity or other out of process
condition.

Referring now to Figure 2, the collected samples are
passed from the sample ports (sample port 10, sample port 74
and sample port 75) to the detector 100 through individual
conduits 90, which typically comprise one-quarter inch
(about 6 mm) diameter flexible stainless steel tubes, which
may optionally be wrapped in heating tape (not shown) in
order to prevent the condensation of gases. The conduits 90
are in fluid communication with the sample ports 10, 74 and
75 and are adapted for fluid communication with the detector
100. While the sample ports may be directly connected to
the detector 100, sample transfer is preferably facilitated
by means of a sample transfer device 91 or other means for
connecting and switching between multiple sample inlets.

The transfer of gases from the sample ports to the
detector 100 may be further facilitated by means of a vacuum
pump 92 having a suction line 93 in fluid communication with
the conduit 90 or sample transfer device 91. The vacuum
pump 92 should preferably be capable of drawing a vacuum of
less than about 10 torr (about 1.5 Pa). The suction line 93
can draw from conduit 90 or sample transfer device 91 to
pass a sample to the detector 100. The suction line 93
preferably draws from the sample transfer device 91 between
first and second detector sample orifices 94, 95 which
regulate the sample flow rate to the detector 100. While a
single sample orifice configuration can be used, in some
embodiments the double sample orifice configuration depicted
in Figure 2 is a preferred system for pressure reduction and
is preferably used in conjunction with a continuous flow

sample stream bypass. The pressure between the first and
second sample orifices 94, 95 is preferably maintained at
about 500 mtorr (about 65 Pa) to provide a sufficient
pressure differential to transfer the detector sample from
the sample port 10 through the conduit 90 to the detector
100. An orifice size of about 1 μm can be used in the
second sample orifice 95. The size of the first sample
orifice is not narrowly critical, but preferably ranges from
about 10 μm to about 5 mm. The sample system is preferably
regulated to obtain a constant mass flow rate of gas through
the sample port 10 and a constant pressure between the
sample orifices 94, 95. Under such conditions, the detector
sample enters the detector 100 with a constant volumetric
flow rate.

Generally speaking, the sampling system is designed to
allow for sampling of the furnace and exhaust gases at
temperatures and pressures common for Cz-types of single
crystal silicon growth processes, by means of commercially
available atmospheric sampling valves. Typically, however,
the pressure within the crystal puller during sample
collection ranges from about 2 to about 50 torr, from about
5 to about 40 torr, or even from about 10 to about 30 torr,
while the temperature ranges from about ambient temperature
to about 1400°C (or more, given that "hot spots" within the
growth chamber can occur in some areas, at times reaching
1500°C, 1600°C, or even 1700°C). More specifically,
suitable detectors 100 for monitoring the composition of the
gaseous atmosphere above the melt or the exhaust gases from
the crystal growth chamber, and/or quantifying the amount of
a particular gas therein, include commercially available
mass analyzers and gas chromatographic detectors, with mass
analyzers being preferred in some embodiments. A
particularly preferred detector is a closed (or enclosed)
ion source quadrupole gas mass analyzer, having a mass range
of about 1 to about 100 amu and a minimum detectable partial
pressure of about 5×10^{-14} torr (using an electron multiplier

detector). Such a gas mass analyzer typically operates at pressures ranging from about $1x10^{-4}$ torr ($1.3x10^{-2}$ Pa) to about $1x10^{-2}$ torr (1.3 Pa) in their ionizing section, and at pressures ranging from about $1x10^{-6}$ torr ($1.3x10^{-4}$ Pa) to

5   about $1x10^{-4}$ torr ($1.3x10^{-2}$ Pa) in their detecting section. An example of a suitable detector is a residual gas analyzer (RGA) such as a Qualitorr Orion Quadrupole Gas Mass Analyzer System (available from MKS, UTI Division of Walpole, Massachusetts).

10   The detector is preferably adapted to detect and quantify the amount of a contaminant gas (e.g., nitrogen, oxygen, water vapor, carbon monoxide) within the collected sample, and thus within the gaseous environment from which the sample was obtained. Additionally, a process purge gas

15   (e.g., argon) is sampled, particularly as a standard to quantify the amounts of the other gases present. For example, in a particularly preferred embodiment wherein the detector is a RGA as described above, it is preferred to monitor N_2 at 14 atomic mass units (amu), monitor O_2 at 32

20   amu, monitor H_2O at 17 amu, monitor CO at 28 amu and monitor Argon by measuring Ar isotope 36 at 36 amu. As used herein, atomic mass units are equivalent to the particular species molecular weight divided by the charge on the molecule, with the charge on the molecule determined by the ionizer in the

25   RGA. The ionizer may also crack or doubly charge the molecules upon entering the RGA. In any case, the amu for each species of interest should be selected so as to reduce any interference between other major species in the furnace and exhaust gases. In this regard, it has been found to

30   preferably monitor for the presence of H_2O at 17 amu rather than 18 amu to reduce any possible interference with doubly-charged Argon 36. Likewise it is important to note the presence of N_2 at 14 amu to determine if CO should be monitored at 28 amu. If N_2 is present at 14 amu, it is

35   important to look for C at 12 amu to detect the presence of CO so as to minimize any interference with N_2 at 28 amu.

The detector 100 communicates with a PLC or PC furnace control system by means common in the art, such as through a system of open and closed switches or through RS232 or RS485 serial ports. The detector can be instructed by the PLC or PC furnace control system to monitor the gases at desired times and locations (as described herein). The detector 100 outputs a detector signal (e.g., electrical current, voltage, etc.) which is physically representative of, corresponds to or can be correlated to the amount of a particular gas in the furnace chamber or furnace exhaust sample. The detector signal output is communicated, directly or indirectly, to the microprocessor 200. The microprocessor 200 may monitor, display, record or further process the detector signal. In the particularly preferred embodiment wherein the detector is an RGA as described above, the detector signal is converted in the microprocessor to equivalent partial pressures or concentrations of the sampled gases, for example, as follows:

$$N_2 \text{ (ppmv)} = 0.042 \times I^{14 \text{ amu}} / I^{36 \text{ amu}} \times 1,000,000 \text{ ppmv}$$

$$O_2 \text{ (ppmv)} = 0.0034 \times I^{32 \text{ amu}} / I^{36 \text{ amu}} \times 1,000,000 \text{ ppmv}$$

$$H_2O \text{ (ppmv)} = 0.01478 \times I^{17 \text{ amu}} / I^{36 \text{ amu}} \times 1,000,000 \text{ ppmv},$$

$$CO \text{ (ppmv)} = 0.0034 \times I^{28 \text{ amu}} / I^{36 \text{ amu}} \times 1,000,000 \text{ ppmv}$$

where $I^{xx \text{ amu}}$ is the current measured by the RGA detector at xx amu.

Preferably, the detector signal is transmitted or otherwise communicated, directly or indirectly (e.g., through a microprocessor 200), to a controller 300. Any standard controller may be employed, including, for example, analog proportional (P), proportional-integral (PI) or proportional-integral-derivative (PID) controllers, digital

controllers approximating such analog P, PI or PID
controllers, or more sophisticated digital controllers. A
digital PID controller is preferred. Such a digital
controller 300 can itself comprise a microprocessor, or can
5   comprise a portion of a larger microprocessor 200. The
controller 300 may also communicate, directly or indirectly,
with a separate microprocessor 200 to provide user input to
the controller, data collection, alarm indications, process
control tracking, etc. The controller 300 (or
10   microprocessor 200) may modify the received detector signal
for use in calculating the changes in process conditions,
for user-interface or for data acquisition or display.

The controller 300 generates a control signal based on
the detector signal (either as received from the detector
15   100 or as modified by the microprocessor 200 or controller
300). In a preferred application, the controller converts
the detector signal to a control signal by applying a
control law based upon the conditions necessary for
controlling the automatic start-up of the crystal furnace
20   heater. Generally, this control law may be based on
theoretical and/or empirical considerations. The control
law used in a particular situation varies depending on the
process condition and on the type of process control element
being manipulated. The control signal generated by the
25   controller 300 may be of a variety of types (e.g., pneumatic
or electrical), and can be transmitted or otherwise
communicated, directly or indirectly, to a process control
element 400 which changes at least one process condition. A
control signal can also be communicated to the process
30   control element 400 via the microprocessor 200 (dashed line
in Fig. 2).

In view of the foregoing, the present invention will be
discussed hereafter in particular detail in regard to
operating protocols associated with conducting an automated
35   pre-fire vacuum integrity test and for general monitoring
during crystal growth to detect out of process conditions.

It is to be noted, however, that the process of the present
invention may be carried out using a system design other
than herein described. For example, multiple crystal
pullers may be connected to a single RGA monitoring system
(e.g., 2, 3, 4 or more).

Pre-Fire Vacuum Integrity Check

In the practice of one embodiment of the present
invention, the crystal growth process is begun by loading a
crucible, contained within a growth furnace or chamber of a
crystal pulling apparatus, with an initial charge of a
semiconductor raw material (e.g., chunk and/or granular
polysilicon) and attaching a seed crystal to the crystal
pulling system. The furnace is then closed and sealed. The
furnace control system is instructed to begin the pre-fire
vacuum check. The inert purge gas (e.g., argon) inlets are
closed and the main exhaust valve is opened and the air is
pumped from the furnace. When the pressure has been
sufficiently reduced, typically to a pressure of less than
about 200 mtorr (e.g., about 190, 170, 150 torr or less),
the main exhaust valve is closed, the purge inlet is opened
and the furnace is filled with a process purge gas, for
example argon (Ar), to a pressure of about 100 torr (e.g.,
about 75, 85, 95, 105, 115 or about 125 torr). The cycle of
reducing the pressure and then back-filling with an inert
process gas is repeated about two additional times. After
the third cycle, the furnace is back-filled to a pressure
ranging from about 2 to about 50 torr (e.g., about 5, 10,
15, 20, 25 torr or more), and the process gas inlets and
main exhaust valves are balanced to maintain a flow rate
ranging from about 15 to about 100 slm (standard liters per
minute or liters per minute adjusted for standard
temperature and pressure), typically about 20, 40, 60 or
even about 80 slm, through the pull chamber, the growth
chamber and the exhaust piping.

Generally speaking, once the growth chamber has been
sufficiently purged, the gaseous environment is sampled and
analyzed about once every 20 minutes, 15 minutes, 10
minutes, 5 minutes or even every minute. Preferably,
however, sampling and analysis will occur on a continuous
basis. In a particularly preferred embodiment, this is
achieved by automated means. For example, when automated,
the furnace control system instructs the detector to monitor
the gaseous environment within the crystal puller (e.g., the
atmosphere over the silicon melt and/or the crystal puller
exhaust) at each port (sequentially or, depending upon the
number of detectors and/or the system configuration,
simultaneously). If the partial pressure of one or more,
and typically if the partial pressure of all, contaminant
gases of interest (e.g., N_2, O_2 and/or H_2O) are below an
acceptable limit, or alternatively within an acceptable
range, the furnace control system allows the heaters in the
growth chamber to be energized in order to begin
heating/melting the polysilicon charge. Generally speaking,
this "pre-fire" check may last a few minutes (e.g., about 2,
4, 8, 10 minutes or more), a few tens of minutes (e.g.,
about 10, 20, 30, 40 minutes), or more with sample
collection and analysis continuing throughout this time
frame, or over only a portion thereof.

The sampling and analysis of the gaseous environment
will generally continue until it has been determined that it
is suitable for crystal growth to be initiated (i.e., for
the furnace heater(s) to be "fired"). Based upon experience
to-date, it has been found that the furnace heater may
typically be started automatically when the gaseous
environment within the growth chamber above and/or adjacent
to the crucible (Port 1) has a contaminant gas
concentration, for example, of less than about 100 ppmv of N_2
(e.g., less than about 80 ppmv, 60 ppmv, 40 ppmv, or even 20
ppmv); less than about 30 ppmv of O_2 (e.g., 25 ppmv, 20 ppmv,
15 ppmv, or even 10 ppmv); and/or, less than about 200 ppmv

of H_2O (e.g., 175 ppmv, 150 ppmv, 125 ppmv, or even 100
ppmv). However, in those instances where the concentration
of a contaminant gas is in excess of the noted limit (i.e.,
the automatic starting values), the crystal furnace operator
may optionally override the monitoring system and manually
start the crystal furnace heater. For example, such actions
may be taken when the concentration of N_2 ranges from about
100 to about 600 ppmv (e.g., from about 150 to 550 ppmv,
about 200 to about 500 ppmv, or about 250 to 450 ppmv), the
concentration of O_2 ranges from about 30 to about 100 ppmv
(e.g., from about 40 to 90 ppmv, or about 50 to 80 ppmv),
and the concentration of H_2O ranges from about 200 to about
1000 ppmv (e.g., from about 300 to 900 ppmv, about 400 to
800 ppmv, or about 500 to 700 ppmv). For concentrations of
N_2 above about 600 ppmv, O_2 above about 100 ppmv, and H_2O
above about 1000 ppmv, the furnace control system will
typically require restarting the pre-fire vacuum check.

Although optional in some embodiments, when exhaust
sampling is employed (e.g., from the RHS pipe (Port 2) and
the LHS pipe (Port 3)), the furnace control system will
typically start the furnace heater automatically if the
concentration of N_2 is less than about 50 ppmv (e.g., less
than about 40, 30, or even 20 ppmv), the concentration of O_2
is less than about 10 ppmv (e.g., less than about 8, 6 or
even 4 ppmv), and the concentration of H_2O is less than about
200 ppmv (e.g., less than about 175 ppmv, 150 ppmv, 125
ppmv, or even 100 ppmv). For concentrations exceeding these
automatic starting values, the crystal furnace operator may
override the monitoring system and manually start the
crystal furnace heater when the concentration of N_2 ranges
from about 50 to about 100 ppmv (e.g., from about 60 to 90
ppmv, or about 70 to 80 ppmv), the concentration of O_2 ranges
from about 10 to about 20 ppmv (e.g., from about 12 to 18
ppmv, or about 14 to 16 ppmv), and the concentration of H_2O
ranges from about 200 to about 1000 ppmv (e.g., from about
300 to 900 ppmv, about 400 to 800 ppmv, or about 500 to 700

ppmv). For concentrations of N_2 above 100 ppmv, O_2 above 20 ppmv and H_2O above 1000 ppmv, the furnace control system will typically require restarting the pre-fire vacuum check.

In this regard it is to be noted that, in some instances, the initial water concentration (i.e., the water concentration prior to the "firing" of the heaters) may be ignored; that is, in some instances, the growth process may be initiated when the water vapor concentration is in excess of 1000 ppmv. Generally speaking, this is because, in a crystal puller at ambient temperature, a significant amount of water vapor can be present on, for example, the surfaces of the graphite parts. Given that the puller is rapidly heated to a temperature in excess of that which causes water to vaporize, this initial presence of water can be quickly reduced.

It is to be further noted that, in some instances, the vacuum integrity of the crystal puller is monitored by means of analyzing the gaseous environment within the crystal puller for the presence of all of the above-referenced contaminant gases, while in other instances the environment will be analyzed for the presence of only one or two of the gases. Additionally, it is to be noted that the inert process or purge gas employed may contain trace levels of one or more of the contaminant gases, levels which are acceptable for purposes of the present invention. Accordingly, generally speaking, the process of the present invention enables the *automated* "firing" of the crystal puller when the concentration of nitrogen ranges from about 5 ppmv to less than about 50 ppmv or 100 ppmv (depending upon whether the concentration in the exhaust gas or above/adjacent to the melt surface, respectively, are being considered), when the concentration of oxygen ranges from about 2 ppmv to less than about 10 ppmv or 30 ppmv (again, depending upon whether the concentration in the exhaust gas or above/adjacent to the melt surface, respectively, are

being considered), and when the concentration of water
ranges from about 2 ppmv to less than about 200 ppmv.

It is to be still further noted that while the
concentration levels provided above are generally applicable
to semiconductor growth processes, the "critical" levels for
initiating growth may be other than described herein without
departing from the present invention. Specifically, from
one crystal puller or crystal pulling process to another,
the unacceptable level of one or more contaminant gases may
vary. As a result, it is preferred to employ means common
in the art, such as statistical process control, to
determine a "baseline" for each process condition or
contaminant gas level which is "typical." Such an approach
generally involves conducting a series of pre-fire tests,
and optionally a series of complete growth cycles, while
monitoring the growth conditions in order to identify
typical or ordinary conditions. A "window" of acceptable
conditions is then established; that is, some degree of
variation (e.g., about 2%, 4%, 6%, 8%, 10%, etc.) is then
allowed, beyond which the crystal puller operator is
notified that an atypical condition is present. A common
approach, for example, is to conduct a series of
statistically significant tests to establish a median level
for each contaminant gas of interest, and then allow a range
of: (i) median plus, or in some cases minus, two times the
standard deviation, (ii) median plus, or in some cases
minus, three times the standard deviation, or (iii) median
plus, or in some cases minus, some multiple of the standard
deviation in excess of three (e.g., 4, 5 or more). In this
way, the present process may be "tuned" to optimize the pre-
fire or growth conditions for any crystal puller or crystal
pulling process.

In a preferred embodiment, the concentration of a
contaminant gas is determined at multiple locations (e.g.,
above and/or adjacent to the melt surface and/or in one or
more of the exhaust gas ports), before the heaters of the

crystal puller are "fired" and meltdown is begun. As
discussed further below, sampling in multiple locations is
beneficial for a number of reasons. For example, depending
upon design of the growth chamber, gas flow through the
chamber may not be uniform. As a result, regions having
different gas compositions within the chamber may be
present. Additionally, the vacuum integrity of the crystal
puller may be compromised in a number of different ways,
each of which may occur in a localized area, again depending
upon the design of the crystal puller/crystal growth
chamber. These factors should be kept in mind when
optimizing (either by empirical means, or by gas flow models
common in the art) sample port placement, the number of
sample ports to be employed, sampling frequency, etc.

Monitoring During Crystal Growth

In a second embodiment of the present invention, during
the semiconductor growth process (i.e., once meltdown has
begun), gases within the growth chamber above and/or
adjacent to the silicon melt surface, and/or the gases in
the exhaust from the chamber, are periodically sampled and
analyzed, in order to monitor the vacuum integrity of the
crystal puller, as well as to monitor the growth chamber for
the presence of other problems which may develop during the
growth process (e.g., failure of a purge gas valve, break or
leak in a water jacket, build-up of carbon monoxide
resulting from the reaction between silicon oxide with
various graphite parts, etc.). The gaseous environment with
the growth chamber is sampled and analyzed for the presence
of a contaminant gas (e.g., oxygen, nitrogen, water vapor,
carbon monoxide) in a concentration in excess of some
predetermined limit.

The timing of sample collection (e.g., when sampling
begins, ends, duration between each sample taken, the number
of samples taken during the process, etc.), as well as the
location and number of sampling points, will generally be

that which is sufficient to ensure representative data of
the crystal puller environment is provided throughout the
growth process. More specifically, however, sampling for
this phase of the present process typically begins as soon
as the heaters have been "fired" and initiation of the
meltdown has begun, in order to ensure no leaks are present
prior to initiation of the semiconductor growth process.
Sampling can continue throughout the entire course of
crystal growth (e.g., from initiation of meltdown until the
end-cone is detached from the melt, or even longer, such as
until cool-down of the puller has occurred). Alternatively,
sampling may occur over only a portion of this time frame
(e.g., during meltdown, growth of the neck or crown, growth
of about 20%, 40%, 60%, 80% or about all of the main body,
growth of the end-cone, etc.). Regardless of the time frame
over which sampling occurs, during the growth process,
sample collection and analysis typically occurs at Port 1,
and optionally at Ports 2 and 3, about once every 20
minutes, 15 minutes, 10 minutes, 5 minutes, or every minute,
or even on a continuous basis.

In this regard it is to be noted that the timing for
sampling may be other than herein described without
departing from the scope of the present invention. For
example, sample collection/analysis may vary depending upon
the growth conditions employed, the type of semiconductor
material to be formed, the design of the crystal pull
apparatus, etc. Generally speaking, however, the timing for
a given puller, process, type, etc. may be optimized
empirically, for example, by growing a number of different
crystals and varying the point at which sample collection
begins and ends, how often samples are taken, the number of
samples taken, etc.

Generally speaking, when the presence of a contaminant
gas is detected at a concentration in excess of the
"background" concentration (i.e., at a concentration in
excess of the typical concentration, as described further

herein, such as the concentration at which the particular
contaminant gas of interest is present in the process or
purge gas being used), or alternatively when it is detected
at a concentration at or nearing some unacceptable
concentration, the growth process can be halted, in order to
avoid the growth of a segment of a semiconductor ingot
(e.g., single crystal silicon ingot) that is not suitable
for use. In such cases, the grown ingot can be further
processed without concern of an unacceptable segment being
present, as the result of an "out of process" condition or
an atypical crystal puller leak. The crystal puller can
then be immediately examined to identify the source of the
contaminant gas, thus limiting "down time" for the crystal
puller.

Additionally, if the "out of process" contaminant level
is set sufficiently low, the growth process can be continued
while the gas level is monitored until just before a
"critical" level is reached, at which point growth must be
halted to prevent the formation of an unacceptable material.
In such instances, corrective actions may be attempted,
(e.g., the source of the leak may be located and repaired)
during the growth process. Alternatively, other attempts
can be taken to prolong the growth cycle, such as, for
example, by increasing the flow of an inert purge gas into
the crystal puller and/or thereby increasing the flow of
exhaust gas out of the crystal puller. In this way, the
concentration of the contaminant gas can be diluted or
suppressed for a period of time.

In accordance with the process of the present invention,
losses in the vacuum integrity of the crystal growth chamber
(such as by leaks), and additionally changes in process
conditions (i.e., "out of process" conditions) resulting
from other sources (e.g., silicon oxide reacting with
graphite parts within the growth chamber), are detected by
closely monitoring, and preferably continuously monitoring,
the composition of the gaseous environment within the

chamber, and/or the composition of the exhaust gases from the chamber. More specifically, as described above, after the crystal puller is sealed, the pressure therein is reduced and the sealed chamber is repeatedly purged with an inert process or purge gas in order to lower the concentration of contaminant gases to below some acceptable level. For example, the system may be purged to lower the concentration of nitrogen to less than about 600 ppmv, 400 ppmv, 200 ppmv, or even 100 ppmv; to lower the concentration of oxygen to less than about 100 ppmv, 90 ppmv, 60 ppmv, or even 30 ppmv; and to lower the concentration of water to less than about 1000 ppmv, 800 ppmv, 600 ppmv, 400 ppmv or even 200 ppmv. Once this has been achieved, and the silicon meltdown and/or ingot growth has begun, the gaseous environment within the crystal puller will be monitored for gas concentrations in excess of these amounts.

In this regard it is to be noted that the inert process or purge gas employed may contain trace levels of one or more of the contaminant gases, levels which are acceptable for purposes of the present invention. Accordingly, generally speaking, the process of the present invention allows for ingot growth to continue when the concentration of nitrogen in the gaseous environment ranges from about 5 ppmv to less than about 600 ppmv (e.g., from about 25 to 400 ppmv, about 50 to 200 ppmv, or even about 75 to 100 ppmv), when the concentration of oxygen ranges from about 2 ppmv to less than about 100 ppmv (e.g., from about 10 to 90 ppmv, about 15 to 60 ppmv, or even about 20 to 30 ppmv), and when the concentration of water vapor ranges from about 2 ppmv to less than about 1000 ppmv (e.g., from about 25 to 800 ppmv, about 50 to 600 ppmv, about 75 to 400 ppmv, or even about 100 to 200 ppmv).

It is to be further noted that, unlike the "pre-fire check," the gaseous environment is also sampled and analyzed for the presence of carbon monoxide; that is, because carbon monoxide begins to form only after the growth chamber is

heated, the concentration of carbon monoxide in the gaseous
environment within the crystal puller is a concern only
after the "pre-fire check" has been completed. Generally
speaking, because carbon monoxide is essentially a by-
product of the growth process (e.g., the result of a
reaction between the silicon dioxide crucible and the
graphite susceptor), the gaseous environment will be
monitored for a concentration which is in excess of a
"background" concentration, with corrective action being
taken or the growth process being halted when concentrations
that would result in "carbon doping" of the melt occur.
Although the concentration will vary with the location of
the sampling port P1 (i.e., the port sampling the atmosphere
above or adjacent the melt), the "background" concentration
of carbon monoxide typically ranges from a few ppmv (e.g.,
about 2, 4, 6, 8, 10 ppmv or more) to several ppmv (e.g.,
about 15, 20, 25, 30 ppmv or more). In contrast, carbon
monoxide concentrations below the melt (i.e., in the lower
regions of the crystal growth chamber, generally below the
crucible) are typically quite higher. Thus, the
concentration of carbon monoxide in the exhaust port samples
will typically be several tens of ppmv (e.g., about 20, 40,
60, 80, 100 ppmv or more). Just as melt doping can be a
concern when the carbon monoxide concentration above the
melt is elevated (e.g., at concentrations in excess of about
30 or 40 ppmv), elevated concentrations below the melt
(e.g., at concentrations in excess of about 100 or 150 ppmv)
can be a strong indication of problems within the pull
chamber (such as a water leak below the crucible), even when
the concentration above the melt is not out of the ordinary
or is below an acceptable limit. Such information is
beneficial, for example, in more precisely determining when
crystal puller maintenance is needed.

It is to be still further noted that while the
concentration levels provided above are generally applicable
to semiconductor growth processes, the "critical" levels for

the growth process may be other than described herein
without departing from the present invention. Specifically,
from one crystal puller or crystal pulling process to
another, the unacceptable level of one or more contaminant
gases may vary. As a result, it is preferred to employ
means common in the art, such as statistical process
control, to determine a "baseline" for each process
condition or contaminant gas level which is "typical." Such
an approach generally involves conducting a series of growth
cycles, while monitoring the growth conditions in order to
identify typical or ordinary conditions. A "window" of
acceptable conditions is then established; that is, some
degree of variation (e.g., about 2%, 4%, 6%, 8%, 10%, etc.)
is then allowed, beyond which the crystal puller operator is
notified that an atypical condition is present. A common
approach, for example, is to conduct a series of
statistically significant tests to establish a median level
for each contaminant gas of interest, and then allow a range
of: (i) median plus, or in some cases minus, two times the
standard deviation, (ii) median plus, or in some cases
minus, three times the standard deviation, or (iii) median
plus, or in some cases minus, some multiple of the standard
deviation in excess of three. In this way, the present
process may be "tuned" to optimize the growth conditions for
any crystal puller or crystal pulling process.

Such an approach is advantageous for a number of
reasons. For example, the particular gas or gases of
concern may vary depending upon, for example, the type of
material being grown, the type of crystal puller, the
location of the crystal puller, the source or type of
process purge gas being employed, etc. Growth conditions
can also be a factor. For example, higher growth
temperatures tend to cause higher "typical" levels of carbon
monoxide in the crystal puller (higher temperatures increase
the rate of those reactions which produce it). As a result,
a higher process temperature means a higher overall "in

process" level of carbon monoxide is acceptable, in comparison to when a lower process temperature is employed.

Identification of the Type and/or Source of Leak

It is to be noted that the process of the present invention is advantageous over methods commonly employed in semiconductor growth processes for a number of reasons. For example, not only does the present invention enable the time for "pre-fire" testing to be reduced, as well as enabling the early detection of contaminant gases in the crystal puller, but it also provides information regarding the nature of the leak or contaminant source within the puller. For example, if only nitrogen is found to be at elevated levels, one might suspect that the purge gas is contaminated, because an air leak would lead to the presence of oxygen, and probably water vapor, as well. Similarly, if only water vapor is detected at elevated levels, one might suspect a water leak, because an air leak would lead to the presence of nitrogen, as well. In this way the present invention may act to further reduce equipment "down time," because the potential sources of the problem can be prioritized.

Additionally, the location of the port from which samples are collected, as well as the timing of the analysis of those samples, can also be controlled to provide beneficial information. For example, sampling and analyzing the exhaust gases is often preferred in some embodiments because the results, when compared to the results of samples collected above the melt or adjacent to the growing ingot, may help to identify the potential cause of an "out of process" condition or to perform "trouble shooting" to determine if other problems with the puller exist (e.g., problems which do not result in "out of process" conditions). For example, by monitoring the exhaust gases in addition to the gases above the melt or adjacent to the growing ingot,

1.   the cause of an elevated carbon monoxide level (as detected by port(s) 2 and/or 3) might be identified as being caused by a bad heater (i.e., a heater having "hot spots" which increase the reaction between SiO in the gaseous environment and carbon from the graphite heater), if the samples collected and analyzed above the melt show no indication of an oxygen leak; or,

2.   the cause of an elevated nitrogen level above the melt (as detected by port 1) in the absence of oxygen or water, might be identified as an air leak near the bottom of the crystal puller furnace, the oxygen being converted to carbon monoxide or silicon dioxide (which might also be detected by sampling at port 1, or alternatively might be swept out of the puller before being detected).

In any event, depending upon the level of the contaminant gas present, pulling may continue while the level is carefully watched and corrective action is taken. In this way, "trouble shooting" may be carried out while semiconductor growth continues. "Trouble shooting" can also be achieved, for example, by comparing the difference between the concentration of a particular contaminant gas at two different locations. In this way one can monitor for the presence of a difference, or an atypical difference, in the concentrations. One beneficial practice is to compare the levels of carbon monoxide present in samples collected at ports 2 and 3. Typically, any difference will be less than about 20 ppmv, 15 ppmv, 10 ppmv, 5 ppmv or even less than about 2 ppmv (with lower differences corresponding to lower "typical" levels of carbon monoxide present in the furnace; e.g., less than about 100 ppmv, 80 ppmv, 60 ppmv, 40 ppmv, 20 ppmv, or less). In this way, problems in the

crystal puller, such as a blocked exhaust outlet, can be detected.

Carbon Content

Substitutional carbon, when present as an impurity in single crystal silicon has the ability to catalyze the formation of oxygen precipitate nucleation centers. Accordingly, in some embodiments, the process of the present invention enables the close monitoring of the gaseous environment within the crystal puller, such that the carbon content of the semiconductor material that is formed has a low concentration of carbon; that is, the semiconductor material typically has a concentration of carbon which is less than about 5×10^{16} atoms/cm^3, less than about 1×10^{16} atoms/cm^3, or even less than about 5×10^{15} atoms/cm^3.

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EXAMPLES

The following Examples set forth one approach that may be used to carry out the process of the present invention. Accordingly, these examples should not be interpreted in a limiting sense.

Example 1

This example demonstrates the benefit of conducting an automated pre-fire check in accordance with the method of the present invention to test the vacuum integrity of the crystal puller prior to beginning the crystal growth process.

A crystal process development run was begun by loading a crucible with an initial charge of polysilicon and attaching a seed crystal to the crystal pulling system contained within a 300 mm Cz crystal growth furnace as described in Figures 1 and 2, such as that commercially available from Kayex of Rochester, NY. The furnace was closed and sealed and the furnace control system began the pre-fire vacuum check by closing the inert purge gas inlets and opening the main exhaust valve. The furnace was evacuated and placed under vacuum by pumping the air from within the crystal growth environment. When the pressure was reduced to about 200 mtorr, the main exhaust valve was closed, the purge inlet was opened and the furnace was filled with argon (Ar), to a pressure of about 100 torr. This cycle of reducing the pressure and then back-filling with an inert process gas was repeated two additional times. After the third cycle, the furnace was back-filled to a pressure of about 15 torr and the process gas inlets and main exhaust valves were balanced to provide for a flow rate of about 100 slm (standard liters per minute or liters per minute adjusted for standard temperature and pressure) through the pull chamber, the growth chamber and the exhaust piping. The gaseous environment within the crystal puller was monitored for

about 10 minutes, with samples collected at a rate of one about every minute from Port 1, Port 2 and Port 3. The samples were then passed to a Qualitorr Orion Quadrupole Gas Mass Analyzer System (commercially available from the UTI Division of MKS from Walpole, MA) as the detector. Monitoring sample results are shown below in Table 1.

Referring to Table 1, samples taken from the crystal growth chamber (Port 1) and the LHS exhaust (Port 3) were well within the acceptable oxygen and nitrogen content ranges for automatic start-up of the furnace heater. However, monitoring results for N_2 and O_2 in the RHS exhaust (Port 2) were out of range for automatic starting. Because experience has shown it to be very unusual for the RHS and LHS exhaust samples to be different by more than about 10%, the crystal puller operator chose to abort the crystal production run and inspect the crystal growth chamber, wherein it was discovered that a plug of silicon oxide was lodged in the RHS Exhaust pipe. The plug was removed and the run restarted without incident.

In this regard it should be noted, with respect to the water content levels, that as explained above these levels may be high in a crystal puller at ambient conditions. As a result, experience with a given puller may lead to the conclusion that levels in excess of 1000 ppmv are acceptable for start-up, because the levels are quickly reduced once the heaters are "fired" (the water quickly being vaporized and swept out of the crystal puller by the process purge gas flow).

Table 1.
Pre-fire monitoring results.

Sample Port	N_2 (ppmv)	N_2 UCL	O_2 (ppmv)	O_2 UCL	H_2O (ppmv)	H_2O UCL
Port 1	50	100	14	30	623	200
Port 2	70	50	17	10	1417	200
Port 3	14	50	1	10	1181	200

Without monitoring the pre-fire vacuum check conditions with the method of the present invention, the plugged RHS exhaust pipe would not have been discovered prior to beginning the crystal growth process and the run would have commenced with the extreme likelihood of not producing any useable crystal. The plugged exhaust pipe would have caused the purge gases flowing through the growth chamber to be very unevenly distributed around the crystal. Most of the flow would be going to the left-hand side of the furnace. The usual consequences of such a condition is a build-up of oxide particles above the melt on the right-hand side. As the mass of small particles collects together and grows, larger particles will be created and many will become detached. Occasionally, one of these particles may be swept into the melt by gas currents created by the asymmetric flow of purge gas. A large particle of silicon oxide on the melt surface during crystal growth will generally become attached to the growing crystal and cause the loss of zero dislocation structure.

Additionally, an asymmetric flow of purge gases around the crystal will generally result in an increase in the carbon content of the crystal. This occurs because the asymmetric gas flow creates a lower pressure on the lower flow side of the growth chamber and by aspiration draws gases containing carbon monoxide (CO) from the lower portion of the growth chamber to the melt surface. The CO readily reacts with the liquid silicon and increases the carbon content of the melt.

Example 2

Nineteen single crystal silicon growth runs were completed in accordance with the Czochralski process using a 300 mm crystal growth furnace commercially available from Kayex of Rochester, NY in order to demonstrate the utility and value of an automatic carbon monoxide (CO) monitoring

and alarm system. The monitoring system was as described
above and as shown in Figs. 1 and 2 employing a Qualitorr
Orion Quadrupole Gas Mass Analyzer System (RGA)
(commercially available from the UTI Division of MKS,
Walpole, MA). Samples were collected at intervals of one
about every five minutes over the length of the main body of
the ingots, based on the above described protocols. All of
the collected data for each ingot was then averaged, to
determine a single data point for each (as shown in Figs. 3
and 4, further discussed below).

At the start of the experiment, the high CO alarm system
was not yet automated; thus, the crystal puller operator was
required to be vigilant in observing the gas composition
displayed on the RGA video monitor. After 11 runs,
indicated by runs labeled A through K on Figures 3 and 4,
alarm limits (upper control limits or UCL) were set based
upon the measured concentrations of CO above and adjacent to
the melt at Port 1 (P1) and in the exhaust gases at Port 2
(P2) and Port 3 (P3). The alarm limits, as shown in Figures
3 and 4, were set for each port based upon control charting
or statistical process control by setting the UCLs for each
port at a value equal to the mean CO concentration observed
in the first eleven runs plus three times the standard
deviation observed in the same eleven runs.

Figure 4 graphically shows the difference in CO
concentrations at P2 and P3 as compared to the CO
concentrations at P1. The difference in CO at P2 and P3 is
plotted in order to identify a condition of unbalanced purge
flow through the crystal growth chamber and in particular
around the crystal. After the first eleven runs, UCLs for
the difference in CO concentration at P2 and P3 and the CO
concentration at P1 were set. The UCLs were again
calculated as the mean value of the first eleven runs plus
three times the standard deviation associated with the same
eleven runs. The results of Figure 4 show that during body
growth of the crystal in run M, the difference between the

CO concentration at P2 and P3 exceeds the UCL. Since this
was a first time occurrence, no corrective action was
prescribed. However, during the runs after M, the
difference between P2 and P3 CO concentration continued to
increase. Also, starting with run N, the CO in the gas
measured above the melt at P1 increased above the UCL. This
is a condition that would be expected to cause the silicon
melt to increase in carbon composition by reaction of CO in
the gases at the melt surface with the molten silicon. To
substantiate this, carbon measurements were obtained for the
crystal from run O and several crystals from runs with CO
below the UCL. As seen in Figure 5, the carbon in crystal
from run O was higher than in the other crystals.

The typical silicon crystal has a very shiny (highly
reflective) surface when it is removed from the crystal
growth furnace. Portions of the crystals produced between
runs M and P had a flat (not reflective) gray surface.
Photographs of the surface of the crystals from run E (low
CO at P1) and run N (high CO at P1) and a microphotograph of
the SiC crystallites formed on the surface of a crystal
similar to the crystal from run N are given in Figure 6.

The monitoring data from Run N suggested the flow of
Argon in the RHS exhaust (P2) was constricted during the run
causing an unbalance in the Ar purge around the crystal.
The unbalanced purge was diluting the CO in the LHS exhaust
stream monitored by P3. As a consequence of the unbalanced
purge around the crystal, gases containing a high
concentration of CO were being aspirated into the upper
portion of the crystal growth furnace from the lower portion
of the crystal growth furnace by the increased flow
differential between the LHS exhaust pipe and the RHS
exhaust pipe. Corrective action consisting of replacing the
protective linings in the graphite upper sections of the
exhaust pipes was taken before Run Q. As seen in Figs. 3
and 4, the CO concentration at all three sampling ports was

back to normal in Run Q and following. Carbon data
available for Run S was found to be typical.

As experience is gained on out of control situations as
represented by this example, corrective actions or
preventive maintenance schemes can be developed to optimize
process performance to improve crystal quality and reduce
manufacturing costs.

<u>Example 3</u>

Sixteen crystal growth runs were conducted in accordance
with the Czochralski process using a 300 mm crystal growth
furnace commercially available from Kayex of Rochester, NY
in order to demonstrate the utility and value of an
automatic monitoring and alarm system for detecting nitrogen
and/or oxygen resulting from, for example, a leak. The
monitoring system was as described above and as shown in
Figs. 1 and 2 employing a Qualitorr Orion Quadrupole Gas
Mass Analyzer System (RGA) (commercially available from the
UTI Division of MKS, Walpole, MA). Samples were collected
at intervals of one about every five minutes during the
growth process, based on the above described protocols. All
of the collected data for each ingot was then averaged, to
determine a single data point for each (as shown in Figs. 7-
10, further discussed below).

In this example, the alarm system was not yet automated;
thus, the operator was required to be vigilant in observing
the gas composition displayed on the RGA video monitor.
After 11 runs, indicated by runs labeled A through K on
Figs. 7 through 10, alarm limits (upper control limits or
UCL) were set based upon the measured concentrations of
nitrogen above and adjacent to the melt at Port 1 (P1) and
in the exhaust gases at Port 2 (P2) and Port 3 (P3). The
alarm limits, as shown in Figs. 7 through 10, were set for
each port based upon control charting or statistical process
control by setting the UCLs for each port at a value equal

to the mean nitrogen concentration observed in the first
eleven runs plus three times the standard deviation observed
in the same eleven runs.

The runs were completed without incident until Run L.
During Run L, the puller was leak tight at the pre-fire
check as indicated at point number 4 in Figs. 7 and 8.
However, during the growth of the crystal, the operator
noted that a leak was present during the body growth of the
crystal. The leak was observed when Port 1 was monitored
but not Port 2, as indicated at point number 4 in Figs. 9
and 10. The level of N_2 was well above expectation at Port 1
but not above expectation at Port 2. Port 3 was also
monitored but was identical to Port 2. The high
concentration of N_2 at Port 1 but not at Port 2 indicated
that the leak was near sampling port 1. It was suspected
that the leak was in a granular poly feeding mechanism near
port 1. An effort was made to stop the leak but was not
successful. It was decided to allow the crystal cycle to
continue to determine the effect on zero defect growth of a
leak of this magnitude. It was quickly decided that zero
defect crystal could not be produced due to the leak and the
cycle was terminated.

In three crystal growth cycles prior to L and one
following L, N_2 was noted to be above expectation during the
pre-fire check with the RGA (see points 1, 2, 3 and 5 in
Figs. 7 and 8). Corrective action was taken before crystal
growth, and as a result of the corrective action, no leak
was observed during crystal growth as indicated by points 1,
2, 3, and 5 in Figs. 9 and 10.

Without monitoring the gases at Port 1 with the RGA, an
air leak would not have been identified as the cause of the
failed crystal growth cycle. In this case, the information
on the leak from the RGA and the failure to grow a zero
defect crystal, led to the decision to shorten the cycle and
save valuable time which was used to begin the next cycle.

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In view of the above, it will be seen that the several
objects of the invention are achieved. As various changes
could be made in the above material and processes without
departing from the scope of the invention, it is intended
that all matter contained in the above description be
interpreted as illustrative and not in a limiting sense.